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Fourier representation methods for Møller–Plesset perturbation theory in one-dimensionally periodic systems

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Abstract

The Fourier representation method developed by Flamant and the present authors for systems periodic in one dimension is used for the first time in ab initio studies that include many-body computations of electron correlation effects. Second-order corrections to the restricted Hartree–Fock energy and energy band gaps are computed in the Møller–Plesset scheme. Systems investigated include H_2, Be, and LiH chains, and comparison is made with direct-space extended-system and oligomer computations. The results confirm the validity of the methods used and illustrate the improvement in convergence relative to direct-space computations.

0. Introduction

Despite the many successes of density functional theory in describing the electronic structure of extended systems, it is limited by its approximate treatment of electron correlation and a lack of systematic procedures for its improvement. A number of studies [1–4] have shown that a more precise accounting of electron correlation is needed to reproduce properties such as band gaps or ionization potentials of extended conjugated systems, and that an improved description of these properties is provided by the second-order Møller–Plesset perturbation scheme, conventionally designated MPBT(2).

Direct-space approaches to ab initio electronic-structure calculations on periodic systems involve lattice sums that are slowly convergent; it has long been known that Hartree–Fock calculations on such systems are prone to numerical errors caused by inappropriate lattice sum truncations [5]. The use of multipole expansions and related techniques [6] have reduced the severity of these convergence problems, but they can be further ameliorated by use of the Ewald procedure [7], which uses Fourier representations and the Poisson summation theorem to convert Coulombic lattice sums into exponentially convergent forms. The application of this Fourier-representation approach to lattices of Gaussian-type orbitals (GTO's) has been developed for one-dimensional periodicity [8–11], and its use was found to be effective in Hartree–Fock calculations, including cases where convergence using direct-space methods was difficult to achieve [12].

Several MBPT(2) computations by direct-space methods have been reported on one-dimensionally periodic systems; see, for example, Refs. [2,3,13,14]. Sun and Bartlett [13] included a study of the convergence behavior of the MBPT(2) correction to the total energy and the band energies, finding that the band structure converges much more slowly than the energy as the extent of lattice summation is increased. This finding underscores the importance of carrying out MBPT(2) computations by methods that have superior convergence properties.

It is the purpose of this Letter to show that the extension of the Fourier-representation approach to the MBPT(2)

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level is practical for periodic systems by reporting here the first such computations and verifying the expected convergence behavior.

1. Method

MBPT(2) computations for closed-shell states of one-dimensionally periodic systems start from the restricted Hartree–Fock (RHF) spatial orbitals $\phi_\mu(k,\mathbf{r})$ and corresponding orbital (band) energies $\epsilon_\mu(k)$, where k, in the range $\left(-\frac{1}{2},\frac{1}{2}\right)$, is a point in the unit-scaled Brillouin zone. The ϕ_μ are Bloch functions, of generic form

$$\phi_\mu(k,\mathbf{r}) = \sum_{m=-\infty}^{\infty} \chi_\mu(k,\mathbf{r} - ma_0\hat{\mathbf{z}})\mathrm{e}^{2\pi imk}, \tag{1}$$

where the periodicity is in the $\hat{\mathbf{z}}$ direction, with cell dimension a_0. In this study the χ_μ are k-dependent linear combinations of spherically symmetric GTO's with centers in a reference cell and with coefficients determined by solving the RHF equations, at a scaling consistent with the formulas presented below. Details have been given elsewhere [10].

In hartree atomic units, the basic formula for $E^{(2)}$, the MBPT(2) correction per unit cell to the RHF energy of a closed-shell system, as written by Pantelides et al. [15], and as used in more recent work [3,13,14] is

$$E^{(2)} = \int_{-\frac{1}{2}}^{\frac{1}{2}} \mathrm{d}k_1 \int_{-\frac{1}{2}}^{\frac{1}{2}} \mathrm{d}k_2 \int_{-\frac{1}{2}}^{\frac{1}{2}} \mathrm{d}k_4 \sum_{ijab} Q_{ij,ab}(k_1;k_2,k_4); \tag{2}$$

the correction $\epsilon_p^{(2)}(k)$ to the band energy for band p (which may be either occupied or unoccupied), at the indicated k value, is

$$\epsilon_p^{(2)}(k) = \int_{-\frac{1}{2}}^{\frac{1}{2}} \mathrm{d}k_2 \times \int_{-\frac{1}{2}}^{\frac{1}{2}} \mathrm{d}k_4 \left[\sum_{jab} Q_{pj,ab}(k;k_2,k_4) + \sum_{ijb} Q_{pb,ij}(k;k_2,k_4)\right]. \tag{3}$$

In these equations i, j and a, b, respectively denote occupied and unoccupied RHF Bloch orbitals. We now introduce the compact notation $\langle k_1k_3\|k_2k_4\rangle_{\mu\nu,\sigma\tau} = \langle\phi_\mu(k_1,\mathbf{r}_1)\phi_\nu(k_3,\mathbf{r}_2) \mid r_{12}^{-1} \mid \phi_\sigma(k_2,\mathbf{r}_1)\phi_\tau(k_4,\mathbf{r}_2)\rangle$ and adopt the convention, dictated by the translational symmetry, that $k_3 = T(k_2 + k_4 - k_1)$. Here $T(k)$ is a function that applies a lattice vector translation if needed to bring its argument k back into the first Brillouin zone. The function Q then assumes the form

$$Q_{\mu\nu,\sigma\tau}(k_1;k_2,k_4) = \frac{|\langle k_1k_3||k_2k_4\rangle_{\mu\nu,\sigma\tau}|^2 + |\langle k_1k_3||k_4k_2\rangle_{\mu\nu,\tau\sigma}|^2 - \mathfrak{Re}[\langle k_1k_3||k_2k_4\rangle^*_{\mu\nu,\sigma\tau}\langle k_1k_3||k_4k_2\rangle_{\mu\nu,\tau\sigma}]}{\epsilon_\mu(k_1) + \epsilon_\nu(k_3) - \epsilon_\sigma(k_2) - \epsilon_\tau(k_4)}. \tag{4}$$

The essence of the Fourier representation method lies in the way in which the matrix elements $\langle k_1k_3\|k_2k_4\rangle_{\mu\nu,\sigma\tau}$ are evaluated. Direct substitution of Eq. (1) and straightforward simplification reduces $\langle k_1k_3\|k_2k_4\rangle_{\mu\nu,\sigma\tau}$ to a three-dimensional sum of atomic two-electron integrals, with the summation in one of the dimensions only convergent as $1/r^2$. However, for a spherical GTO basis, the application of Fourier representation theory in conjunction with the Ewald procedure yields a three-dimensional direct-space sum involving complementary error functions, plus a corresponding reciprocal-space sum involving the incomplete Bessel function $K_0(u,v)$, of definition

$$K_0(u,v) = \int_1^\infty \exp\left(-xt - \frac{y}{t}\right)\mathrm{d}t. \tag{5}$$

Both these sums converge exponentially in all their summation indices, and convenient methods are available for the special functions involved: the error functions are familiar in GTO computations; for $K_0(u,v)$, see Refs. [16,17]. When written in terms of the basis functions, the matrix elements are just those arising in RHF calculations, for which all the necessary formulas have been published elsewhere [10].

For the Fourier-representation calculations, the k integrations in Eqs. (2) and (3) were carried out numerically, using equal numbers of k points in each dimension. One of the integrations in Eq. (2) was evaluated using concatenated nine-point (eight subinterval) Newton–Cotes formulas; the other two integrations, and both integrations in Eq. (3), were performed using a two-dimensional simplex method [18].

Comparison computations using for extended systems the PLH direct-space program [19], and for oligomers GAUSSIAN-03 [20], were made using the procedures built into those respective programs.

2. Results and discussion

We report data on the following linear systems, chosen to illustrate the differences between various computational methods: (1) an H_2 chain, one molecule per unit cell, with the H–H bond length at the equilibrium value of 1.42 bohr and with a cell dimension of 4.00 bohr, corresponding to weakly interacting molecules; (2) a LiH chain, one LiH per unit cell, of cell dimension 6.48 bohr and an LiH bond length of 3.24 bohr (equally spaced atoms), and (3) a chain of equally spaced Be atoms, one per unit cell, with cell dimensions 3.00, 2.75, and 2.50 Å. For H and Li we used standard STO-3 G basis sets (s functions only); for Be we used a DSGF-3-21 G basis [21]. Use of the DSGF basis does not represent a limitation in the method employed here, but was simply a choice facilitating a convenient preliminary study. The RHF calculations were carried out with convergence limits of 10^{-6} in the elements of the den-

sity matrix, and the lattice sums were extended as necessary to be consistent with the convergence limit. All the occupied and unoccupied RHF orbitals were included in the MBPT(2) summations.

An initial test of the formalism is provided by a comparison between extended-system and oligomer results for both the RHF energy and the MBPT(2) correction $E^{(2)}$. Table 1 shows such a comparison for some cases where all the methods give stable, converged results. Oligomer computations were carried out for both linear and cyclic systems for various numbers N of unit cells; the table gives only representative values and the carefully extrapolated infinite-N limits. FTCHAIN refers to the code for the Fourier-representation approach; PLH is a direct-space program. The RHF energies are well converged with respect to the number of k points used in each dimension; the $E^{(2)}$ values are not fully converged with respect to k, and data are given for various numbers of points. The main conclusion to be drawn from Table 1 is that the RHF and MBPT(2) formulas seem to have been properly implemented in the Fourier-representation scheme.

We look next at the band energies for the systems studied in Table 1. Table 2 gives the highest-energy occupied orbital (HOMO), the lowest-energy unoccupied orbital (LUMO), and their difference (the band gap). We note that in general the MBPT(2) correction has a major influence on the calculated band structure. For H_2, the direct-space (PLH) and Fourier-representation (FTCHAIN) methods are in good agreement and the results exhibit only a weak dependence on the number of k-points used in the integrations of Eq. (3). These data confirm the implementation of the HOMO and LUMO computations. However, the data for LiH show significant differences between the PLH and FTCHAIN results, indicative of the fact, previously noted by Sun and Bartlett [13], that a direct-lattice summation extent that is just sufficient for the energy will not be adequate for computations of the one-electron properties. This observation does not really apply to the Fourier-representation method, due to the exponential convergence of its lattice sums.

The Be chains provide an example illustrating the importance of having adequate lattice-sum convergence. Our results (not shown) at unit-cell dimensions 2.75 and 3 Å indicate rapid convergence of the oligomer data to FTCHAIN RHF and MBPT(2) energy values; moreover, the FTCHAIN HOMO, LUMO, and band gap energies are stable and only weakly dependent on the number of k-points. Reasonable agreement is also obtained with direct-space computations. However, at cell dimension $a_0 = 2.50$ Å, where the Be–Be distance is short enough that the GTO basis approaches linear dependence, the situation becomes very different. The RHF equations then become unstable unless the matrix elements $\langle k_1 k_3 \| k_2 k_4 \rangle_{\mu\nu,\sigma\tau}$ are computed to much higher precision than was needed for larger values of a_0, and it becomes more difficult to obtain RHF convergence with a direct-space approach [21].

The Fourier-representation method does not experience any particular difficulty with the situation represented by

Table 1
RHF total energies per unit cell and MBPT(2) corrections $E^{(2)}$ for oligomer, Fourier-representation (FTCHAIN) and direct-space (PLH) computations

		RHF	$E^{(2)}$
H_2	Oligomers[a]		
$a_0 = 4.00$	Δ(50)	−1.100 476 77	−0.013 972 36
	Δ(100)	−1.100 476 76	−0.013 972 36
	Δ(limit)	−1.100 476 76	−0.013 972 36
	FTCHAIN	−1.100 476 77	
	8 k-points		−0.013 971 77
	16 k-points		−0.013 972 26
	32 k-points		−0.013 972 34
	PLH	−1.100 475 89	
	21 k-points		−0.013 973 06
LiH	Oligomers		
$a_0 = 6.48$	Δ(50)	−7.839 515 68	−0.013 218
	Δ(100)	−7.839 527 88	−0.013 218
	Δ(limit)	−7.839 531 78	−0.013 218
	FTCHAIN	−7.839 531 82	
	8 k-points		−0.013 223
	16 k-points		−0.013 225
	32 k-points		−0.013 225
	PLH	−7.839 531 83[b]	
	21 k-points		−0.013 289

Data are in hartree atomic units.
[a] Δ(m) is the energy increment upon adding one unit to an m-unit oligomer.
[b] D. Jacquemin, private communication, using method of Ref. [22].

Table 2
RHF and MBPT(2) band energies and gaps, for computations by Fourier-representation (FTCHAIN) and direct-space (PLH) methods

		HOMO	LUMO	Gap
H_2 ($a_0 = 4.00$)				
FTCHAIN				
RHF		−0.435 70	0.365 20	0.800 90
MBPT(2)	8 k-points	−0.429 44	0.360 39	0.789 83
	16 k-points	−0.429 59	0.360 55	0.790 14
	32 k-points	−0.429 60	0.360 57	0.790 17
PLH				
RHF		−0.435 70	0.365 20	0.800 90
MBPT(2)	21 k-points	−0.429 60	0.360 58	0.790 18
LiH ($a_0 = 6.48$)				
FTCHAIN				
RHF		−0.208 64	0.174 32	0.382 96
MBPT(2)	8 k-points	−0.147 41	0.161 22	0.308 63
	16 k-points	−0.147 59	0.161 40	0.308 99
	32 k-points	−0.147 60	0.161 43	0.309 03
PLH				
RHF[a]		−0.208 64	0.174 32	0.382 96
MBPT(2)	21 k-points	−0.148 71	0.157 45	0.306 16

[a] D. Jacquemin, private communication, using method of Ref. [22].

Table 3
MBPT(2) energy corrections and band energies (in hartree atomic units) for the linear Be chain at interatom spacing 2.5 Å

	$E^{(2)}$	HOMO	LUMO	Gap
RHF		−0.054 92	0.050 67	0.105 59
MBPT(2)				
8 k-points	−0.023 164	−0.053 25	0.006 85	0.060 10
16 k-points	−0.023 337	−0.048 05	0.001 17	0.049 22
32 k-points	−0.023 369	−0.047 68	0.000 80	0.048 48

the Be chain at $a_0 = 2.5$ Å, yielding RHF energy per unit cell −14.475 486 hartree, in excellent agreement with the extrapolated oligomer value. The MBPT(2) results are stable, but more dependent on the number of k-points than in other cases; values of $E^{(2)}$ and band energies are given in Table 3.

3. Perspectives

Summarizing, we point out that the most significant difference between Fourier-representation and direct-space calculations is in the convergence rate of the lattice summations. In the FTCHAIN results presented above, the exponential convergence permitted the accuracy there reported to be typically achieved with four to six terms in each dimension of each summation (thereby totalling for the two three-dimensional summations occurring in the formula for $\langle k_1 k_3 \| k_2 k_4 \rangle_{\mu\nu,\sigma\tau}$ some 200–300 terms). This may be contrasted with the many thousands of terms needed to attain comparable accuracy in the direct-space approach.

The reader has perhaps noted that the advantages of the more rapid lattice-sum convergence may be to some extent offset by the fact that individual terms in the Fourier-representation approach appear more computationally cumbersome than their direct-space counterparts. In that connection it should be kept in mind that the present status of the direct-space approach is the resultant of a substantial investment in its technology, whereas the Fourier-representation methods are still at an early developmental stage. There is thus reason to be optimistic that in the future the Fourier-representation approach may become a method of choice for electronic-structure studies of one-dimensionally periodic systems.

The methods of the present study can be extended to systems with periodicity in larger numbers of dimensions; much of the technology involved is similar to that occurring in the treatment of Ewald acceleration of two- and three-dimensional lattice sums (see, for example, Refs. [23–25]). The present authors hope to soon report some results for surface systems with two-dimensional periodicity.

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